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DISTORTION AND ORIENTATION FOR TRIPLET CORONENE

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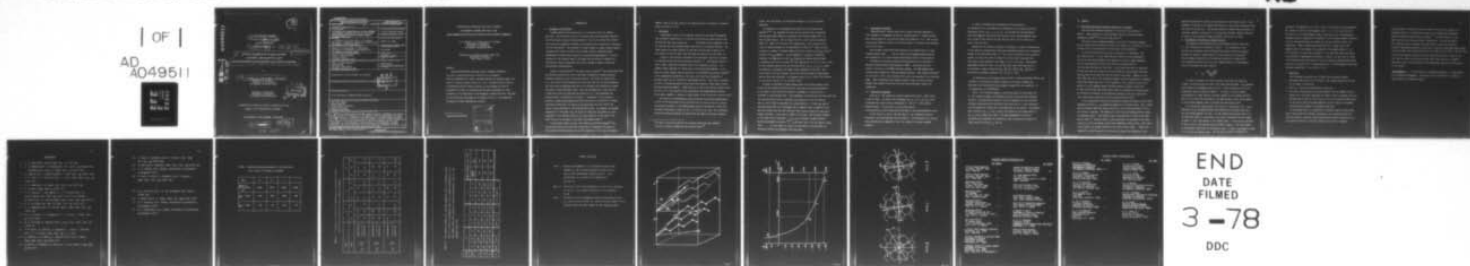
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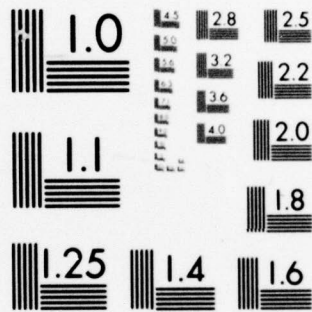
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(15) OFFICE OF NAVAL RESEARCH
Contract No. N00014-75-C-0602

Task No. NR-056-498

(9) TECHNICAL REPORT NO. 28

(14) TR-28

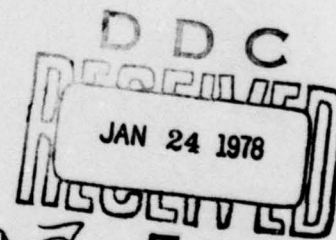
CONTRIB-3918

(6) DISTORTION AND ORIENTATION FOR TRIPLET CORONENE
IN DIFFERENT n-HEPTANE SHPOL'SKII SITES
USING PHOSPHORESCENCE-POLARIZED MICROWAVE DOUBLE RESONANCE TECHNIQUES.

by

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(11) Dec 1977

(12) 20 p.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 28 ✓	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DISTORTION AND ORIENTATION FOR TRIPLET CORONENE IN DIFFERENT n-HEPTANE SHPOL'SKII SITES USING PHOSPHORESCENCE-POLARIZED MICROWAVE DOUBLE RESONANCE TECHNIQUES		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) A. M. Merle, W. M. Pitts and M. A. El-Sayed Department of Chemistry, University of California Los Angeles, California 90024		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Regents of the University of California University of California, 405 Hilgard Ave., Los Angeles, California 90024		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0602 ✓
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Branch Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-056-498
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Branch Office 1030 East Green Street Pasadena, California 91106		12. REPORT DATE December 27, 1977
		13. NUMBER OF PAGES 19
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Distribution of this document is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) <div style="text-align: center;"> DDC RECEIVED JAN 24 1978 RESOLVED F </div>		
18. SUPPLEMENTARY NOTES To be published in Chemical Physics Letters		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Shpol'skii Effect Single Crystals Orientation of Molecules Optical Detection Polarized Microwaves		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>→ Using phosphorescence microwave double resonance techniques, the type of distortion and the orientation of the magnetic axes are determined for triplet coronene molecules in idfferent Shpol'skii sites in n-heptane single crystals at 1.6°K. Coronene triplet molecules in different sites are found to differ one from another not only in orientation but also in the degree and the sense (quinoidal vs. antiquinoidal) of the distrotion of the hexagonal coronene structure. The less is the distrotion, the higher is the energy of the $T_1 \leftrightarrow S_0$ transition. Discussion of these observations is given.</p>		

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DISTORTION AND ORIENTATION FOR TRIPLET CORONENE
IN DIFFERENT n-HEPTANE SHPOL'SKII SITES
USING PHOSPHORESCENCE-POLARIZED MICROWAVE DOUBLE RESONANCE TECHNIQUES

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Abstract:

Using phosphorescence microwave double resonance techniques, the type of distortion and the orientation of the magnetic axes are determined for triplet coronene molecules in different Shpol'skii sites in n-heptane single crystals at 1.6°K. Coronene triplet molecules in different sites are found to differ one from another not only in orientation but also in the degree and the sense (quinoidal vs. anti-quinoidal) of the distortion of the hexagonal coronene structure. The less is the distortion, the higher is the energy of the $T_1 \leftrightarrow S_0$ transition. Discussion of these observations is given.

[†]Contribution No. 3918

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I. INTRODUCTION

A. Statement of the Problem

n-Alkane matrices have been shown to be favorable hosts for aromatic molecules. The electronic spectra of the guest show the quasilinear character and the multiplet structure characteristic of the so-called Shpol'skii effect.¹ This effect was originally observed in polycrystals and a theoretical interpretation has been given.² The extension of these studies to single crystals greatly increased this effect's interest since single crystals constitute three-dimensionally oriented media useful for polarization measurements.³ Both the sharpness of the observed bands of the guest and the ability to measure its polarization characteristics make these hosts extremely useful in molecular spectroscopic investigations.

Studies in polycrystals^{4,5} and single alkane crystals^{6,7} have established that the multiplet structure is due to electronic transitions of guest molecules inserted in distinct sites of the host lattice. The nature of these sites, i.e., the crystal field anisotropy in these sites, has not yet been determined. The first step in attaining this goal is to determine the orientation of guest molecules in these different sites. The only determination of this type in a Shpol'skii matrix has been done by Canters et al.⁷ who determined the insertion mode of porphyrins in n-octane. Furthermore, if one selects a molecule of high enough symmetry and whose structure is susceptible to pseudo Jahn-Teller distortion, the nature of the distortion can also reflect the crystal field anisotropy in the different host sites. For example, using PMDR techniques,⁸ it was found that the nature of distortion (quinoidal vs. anti-quinoidal) of the benzene triplet is not only sensitive to the type of the host⁹ but also to the phase of the same (cyclohexane) host.¹⁰

In the present study, we have used linearly polarized microwaves¹¹ and optical detection of the zero-field transitions to determine the nature of the pseudo Jahn-Teller distortion and the orientation of the three orthogonal

magnetic axes of the $^3B_{1u}$ state of the observed sites of coronene in n-heptane single crystals at 1.6 K.

B. The System

A preliminary study of the n-heptane crystalline structure¹⁰ determined that n-heptane crystallizes in a triclinic $P\bar{1}$ system with angles close to 90° and does not show phase transition. The growth axis is assigned to the (a) axis and only two cleavage planes (ab) and (ac) are usually observed. The alkane chains are almost parallel to the (ab) face and make an angle of 71° with respect to the (a) axis; they are lined up along the (c) axis (Fig. 1).

A study of the multiplet structure of the electronic spectra of coronene in n-heptane lattice has been previously reported.¹³ The emission spectra show a rather complicated structure with a five-component multiplet. The highest energy component (α) exists only in polycrystalline samples. On the basis of various studies such as the effect of annealing⁶ and external pressure¹⁴ on the luminescence properties of the site, site α has been attributed to molecules which are not inserted in the heptane lattice. This line is followed in order of decreasing energy by four lines which appear in both single crystal and polycrystalline samples. A weak line due to the β site and two intense lines for the γ and δ sites exist in both fluorescence and phosphorescence spectra. A very small component ϵ appears to lower energy in the fluorescence spectrum only.*

The results of phosphorescence and fluorescence polarization measurements as well as ESR measurements have concluded that the various sites are related to molecules inserted in the substitutional plane of the lattice so that the molecular plane makes an angle of $70^\circ \pm 10^\circ$ with the (a) axis. No correlation could be established between the optical and the magnetic multiplet observed

* In order to avoid any confusion the coronene sites have been labelled $\alpha, \beta, \gamma, \delta, \epsilon$ instead of AbCDe used in previous papers.¹³

by ESR. For this reason, the distinction between β , γ and δ sites was impossible.

The analysis of the phosphorescence spectrum has previously been reported.^{15,16} The forbidden 0-0 band can be observed with a relatively high intensity which implies a lowering of the coronene symmetry due to crystal field effects. The 0,0 band of the β , γ and δ sites are found at 19405 cm^{-1} , 19383 cm^{-1} and 19350 cm^{-1} respectively. The 0,0 band of the α site is observed weakly in the polycrystal at 19436 cm^{-1} . Built on each 0,0 band is a number of vibronic bands, the first of which is the e_{2g} 370 cm^{-1} vibration (in D_{6h} symmetry). As the symmetry of coronene is lowered in n-heptane, the degeneracy of this e_{2g} vibration is removed and this band is therefore split into two bands of $\sim 4\text{ cm}^{-1}$ separation for the β , γ and δ sites. For this vibronic band we will use the notation β_1 , β_2 , γ_1 , γ_2 , δ_1 , δ_2 , where the subscript 1 represents the higher energy component of the site. The α site which is the most intense line in the vibronic bands of polycrystals does not show this splitting. An extensive study of the crystal field effects on the optical spectra will be published later.

Coronene is believed to remain planar within its insertion modes in the lattice as the crystal structure does not favor any out-of-plane distortion. On the basis of this belief the molecule is assumed to be distorted to a quinoidal or antiquinoidal form. This assumption is supported by the fact that only one zero-field spin level is observed to be radiative to the 0,0 band for the β , γ and δ sites as expected for a planar molecule. In this D_{2h} type of molecular distortion, the orthonormal set of magnetic axes is taken as A,B,N. The A,B in-plane axes are such that the A axis passes through the atoms and B bisects the bonds. The N axis is normal to the plane. The relative ordering of the three triplet sublevels τ_A , τ_B , τ_N of coronene in alkane matrices has been determined previously.^{17,18} τ_A has been found to be the highest energy level. In these works, no results or discussion of the difference in distortion between the different sites was given.

II. Experimental Apparatus

n-Heptane single crystals doped with coronene have been prepared by slow cooling of the degassed solution as reported earlier.³ Single crystals were cleaved along the (ab) and (ac) faces and studied at 1.5 K. The crystals were oriented within an accuracy of 10° with respect to the horn after locating their optical axes.

The coronene triplet state was populated by the 3650 Å line of a high pressure mercury lamp. Selected lines of the phosphorescence spectrum were isolated by a 1 m Czerny-Turner monochromator with 0.41 Å resolution.

The degree of microwave absorption was monitored by the technique of microwave induced delayed phosphorescence (MIDP). Microwaves were provided to the horn by a HP 8690B microwave sweeper. The MIDP signals were collected and averaged on a TMC multichannel analyzer. The studied transitions ($D + |E|$ and $D - |E|$) were recorded 10-20s after the cessation of the exciting light. Their frequencies were measured within ± 2 MHz uncertainty using a Beckman 7580 transfer oscillator and an HP 5245L electronic counter for calibration.

III. Experimental Approach

Only the $D - |E|$ transition could be observed for the β , γ and δ sites of the 0,0 band. For each of the components β_1 , β_2 , γ_1 , γ_2 , δ_1 , δ_2 of the 0,370 band only one of the two transitions $D - |E|$ or $D + |E|$ could be observed easily. On the contrary, both levels appear to be radiative in the 0,0 band and 0,370 bands of the polycrystalline α site.

In the case of γ_1 and δ_1 , the very weak $D - |E|$ transition could be observed at the same frequency as the intense $D - |E|$ transition of γ_2 and δ_2 , thus confirming that components 1 and 2 are related to the same coronene molecule.

In order to determine the orientation of the molecules in the different sites, we studied the polarization of the intense zero-field transitions for β_1 , β_2 , γ_1 , γ_2 , δ_1 , δ_2 . We successively used microwaves with their magnetic field polarized along and across crystallographic axes: the (a) axis in the case of the (ab) and (ac) faces, the (c) axis in the case of the (bc) face.

Because of the triclinic structure of n-heptane, an easier interpretation of the results is obtained when using the orthonormal system (x,y,z) previously defined in the ESR studies (Fig. 1). The x axis is parallel to the crystallographic (a) axis, the y axis is normal to (a) and lies in the (ab) face, the z axis is then defined as the normal to the x and y axes. Polarization measurements along the (ab), (ac) and (bc) faces then yield the ratios of the microwave signal intensities $P_{xy}^{\mu} = \frac{I_x}{I_y}$, $P_{xz}^{\mu} = \frac{I_x}{I_z}$ and $P_{zy}^{\mu} = \frac{I_z}{I_y}$ where μ specifies the microwave transition ($D + |E|$ or $D - |E|$).

At sufficiently low microwave power in order to avoid saturation effects, the intensity of the microwave signal I depends on the angle ϕ between the microwave field direction \vec{H} and the magnetic moment \vec{M} of the transition. It is proportional to $|\vec{H}|^2 |\vec{M}|^2 \cos^2 \phi$.

The $D - |E|$ transition moment is polarized along the A axis while the $D + |E|$ transition moment is polarized along the B axis (see the following section). The polarization ratios of the six components of the 0,370 band determine the directions of both the A and B axes for β , γ , and δ molecules and thus define the orientation of the molecules in the lattice. The measurements related to β_1 , γ_1 , and δ_1 lead to the direction of B while those of β_2 , γ_2 , and δ_2 define the A axis. The same measurements for the 0-0 transition only determine the direction of the A axis and are identical to those found for sites β_2 , γ_2 , and δ_2 .

IV. Results

A. Zero-field Splitting Parameters: Distortion of Coronene

The zero-field parameters measured for each site are reported in Table 1. These values are in good agreement with the values previously determined by MIDP^{17,18} and by the ESR method.¹⁹

The sign of the E parameter depends on the type of distortion induced by the crystal field (positive for quinoid and negative for antiquinoid) and its absolute value is characteristic of the extent of the distortion.

In the 0,0 band only the τ_B level is expected to be radiative. For the three sites β , γ , δ this level has been found to be the intermediate one so the zero-field parameter E is negative for each of these components. For the polycrystalline α site, both levels are radiative due to the very weak distortion of this site. A very small distortion is supported by the facts that site α has a very low intensity in the 0,0 band, the 0,370 band e_{2g} band is not split and its $|E|$ value is very small. However, it has been found that the $D + |E|$ transition appears in the 0,0 band with an intensity three times higher than the $D - |E|$ transition. The τ_B level of site α thus appears to be the highest energy one which implies a positive value of E. We thus conclude that the crystal field effect of n-heptane on coronene favors an antiquinoid distortion of the molecules inserted in the β, γ, δ site and a very slight quinoid distortion for the polycrystalline α site.

It is interesting to study the correlation between the values of the E and D parameters and the $T_1 - S_0$ transition energy for the various sites. Fig. 2 shows this correlation where the energy scales for D and E have been chosen to allow the curves to coincide. The behavior of D and E with decreasing optical energy are amazingly alike. Such behavior might be interpreted in terms of the Jahn-Teller effect.²⁰ The more severe is the distortion, the stronger is the interaction of T_1 with the higher energy doubly degenerate triplet state. This interaction leads to an energy lowering in the lowest triplet state. While this explanation sounds attractive, one should not neglect the difference in the

ground state electronic energy of the molecules in the different sites. The D parameter is related to the spatial distribution of the triplet electrons within the plane of the molecule. The average separation between these electrons will increase, implying a decrease of D , on going from the small quinoic distortion of site α to the relatively large antiquinoic distortion of δ site.

B. Orientation of Coronene in n-Heptane Lattice

The measured ratios defining the in-plane magnetic axes of the three β , γ and δ molecules are reported in Table 2. The orientation of the molecule was calculated from the observed polarization ratios by using an optimization computer program based on a least squares fit procedure.²¹ From an assumed orientation of the molecule defined by its axes A'B'N', this program calculated P'_{ij} ratios, and compared them to the experimental ones by calculating the error function

$$S = \sum_{\mu ij} \frac{(P_{ij}^{\mu} - P'_{ij}{}^{\mu})^2}{(P_{ij}^{\mu})^2}$$

In order to minimize this error function, successive and iterative 2-degree rotations around the three A'B'N' axes were performed. The optimized Euler angles of the magnetic axes of the β , γ , and δ molecules in the x,y,z orthonormal system are given in Table 3. In order to allow an easier interpretation of these results, the Euler angles of the n-heptane molecule and of the (c) axis are also given in the same system, as well as the angle θ of the in-plane magnetic axes of coronene with the heptane chain.

We conclude from these results that within 5° uncertainty the β , γ and δ molecules lie in the substitutional plane defined by the alkane chain axis and the crystallographic (c) axis. In this substitutional plane (Fig. 3) it is found that within 5° uncertainty, the B axis of molecules in site β makes an angle $\theta = \pm 30^\circ$ with respect to the heptane chain. In the case of molecules in site γ , their B axis has been found to make an angle $\theta = \pm 12^\circ$ with respect to the heptane chain while for molecules in site δ , their A axis makes an angle $\theta = \pm 12^\circ$ with the heptane chain. The two main positions of insertion of

coronene in the heptane lattice, site γ and δ , are related by an approximately 90° rotation of their in-plane magnetic axes. It is to be noted that the direction of the in-plane magnetic axes of molecules γ and δ experimentally determined lead to a geometrical orientation of the molecule slightly different from the one expected when only taking into account intuitive steric considerations. These considerations would lead one to expect one of the magnetic axes of the aromatic to be parallel to the heptane chain ($\theta = 0$). It is difficult to prove that the angle $\theta = \pm 12^\circ$ which has been found cannot be attributed to experimental uncertainty. However, the fact that to within 5° the molecules have been found to lie in the predicted substitutional plane allows us to conclude that our measurements have a low experimental uncertainty and gives significance to the value $\theta = \pm 12^\circ$.

V. Discussion

The following conclusions can be drawn from the present studies:

1. The higher the energy of the 0,0 band of the coronene molecules the less is the degree of distortion.
2. Sites β , γ , and δ have antiquinoidal structures.
3. The α -site, observed only in the polycrystals, has the highest 0,0 band energy and is the least distorted, but seems to have a quinoidal structure.
4. The molecules in the β , γ and δ sites all lie in the substitutional plane of the lattice and the in-plane magnetic axes are found to be oriented differently with respect to the alkane chain axes.

It thus seems that by a combination of different types of pseudo Jahn-Teller distortions and different orientations, the coronene molecule can find the different potential energy substitutional minima that give rise to the observed Shopl'skii's multiplet emission structure in n-heptane.

This conclusion is different from that reached concerning the origin of the different sites of the naphthalene x-traps in the naphthalene-tetrachlorophthalic anhydride charge transfer crystals.²² In these crystals, it was found that all the sites have similar orientations. In order for them to have different optical energies, they must then be created by having the different naphthalene molecules located next to different impurities having higher triplet energies (the accepted notion for the origin of the x-trap). The fact that they all have similar orientation in this system must then be a result of the fact that the other host molecules around these traps (and not the impurity molecules) control the orientation of the naphthalene molecules in these sites in the lattice.

Acknowledgments: A. M. Merle wishes to acknowledge Professor J. Joussot-Dubien for continuous encouragement. The authors wish to thank the U. S. Office of Naval Research for financial support.

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Table 1. Zerofield splitting parameters of the four sites
 α , β , γ and δ of coronene in n-heptane.

Site	α	β	γ	δ
Energy in the 0,0 band cm ⁻¹	19436	19405	19383	19350
D _{MHz} \pm 2 MHz	2941	2905	2900	2892
E _{MHz} \pm 2 MHz	+28	-83	-105	-132

Table 2. A comparison between the experimental polarization ratios
with those calculated by least squares procedure

Site	β			γ			δ		
Axes	A	B	N	A	B	N	A	B	N
$P_{xy} = \frac{I_x}{I_y}$	experimental	.18	.32	4.8	.12		.04	1.9	
	calculated	.16	.27	5.3	.12	5.4	.05	2.1	11
$P_{xz} = \frac{I_x}{I_z}$	experimental	.08	.86	.14	3.5		3.8	.08	
	calculated	.09	.76	.13	1.5	11	1.1	.06	24
$P_{zy} = \frac{I_z}{I_y}$	experimental	2.8	.35	20	.06		.08	30	
	calculated	1.7	.36	42	.08	.47	.05	35	.49

Table 3. The angles between the coronene magnetic axes in different sites and: i) a set of orthogonal axes x,y,z (whose orientation w.r.t. the alkane chain and crystal \vec{c} axis is also given), and ii) the heptane chain (θ).

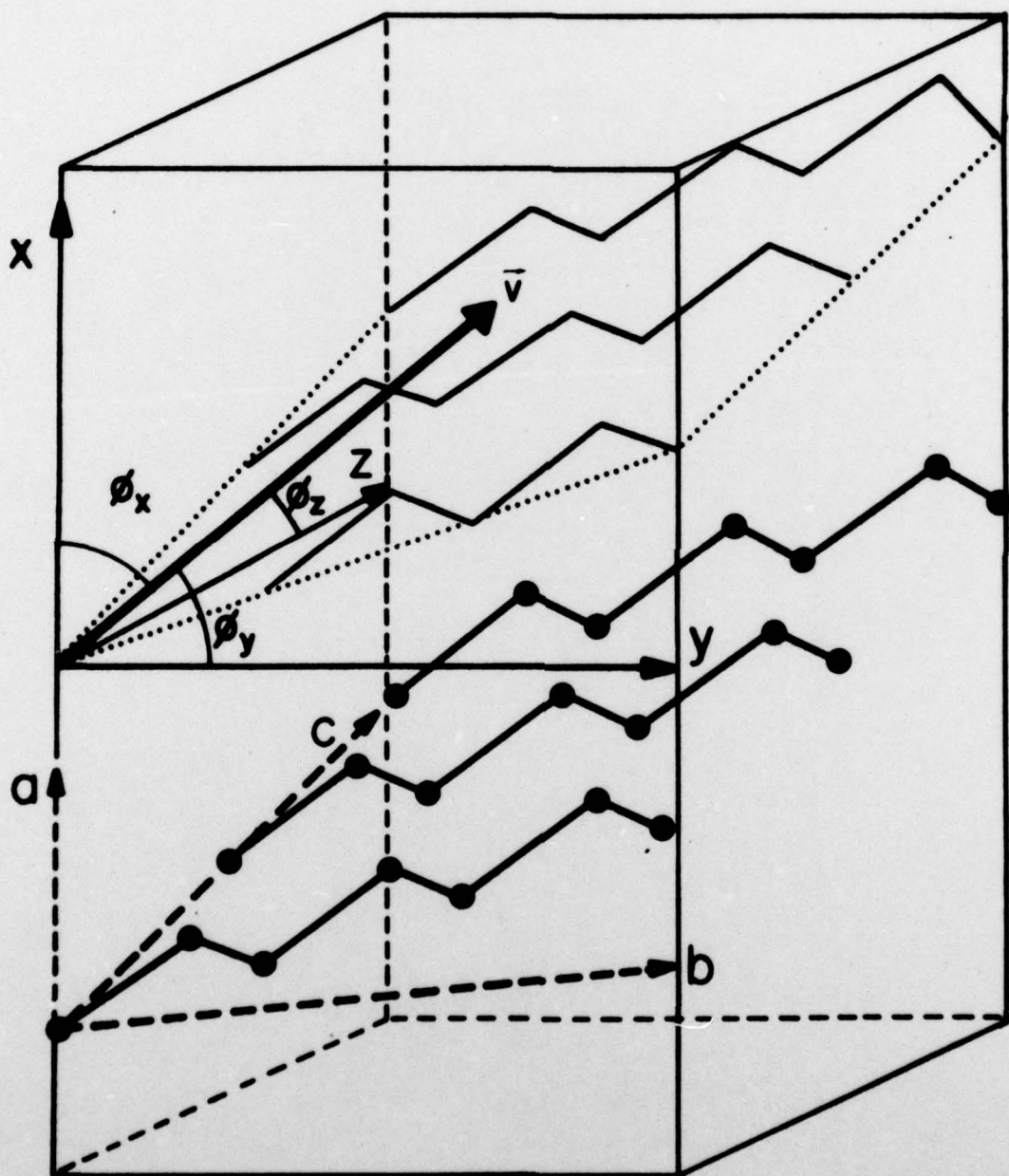
Site	β			γ			δ			Angle between x,y,z and:	
	A	B	N	A	B	N	A	B	N	Alkane chain	\vec{c} axis
ϕ_x	76°	66°	28°	70°	71°	27°	76°	76°	19°	71°	74°
ϕ_y	126°	38°	101°	81°	24°	112°	18°	80°	105°	19°	92°
ϕ_z	39°	62°	115°	21°	105°	105°	102°	17°	101°	92°	16°
θ	123°	31°		102°	13°		12°	102°			

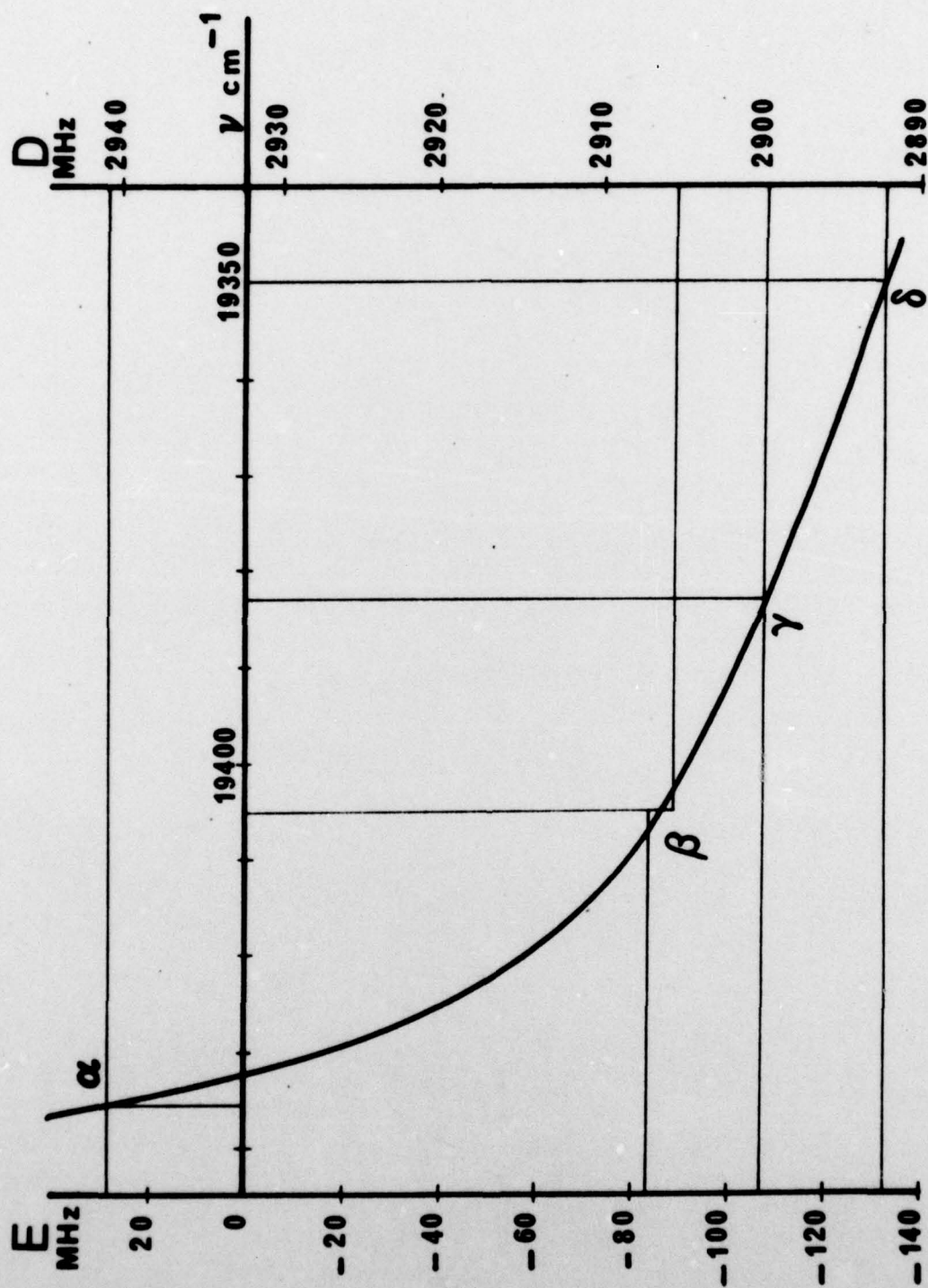
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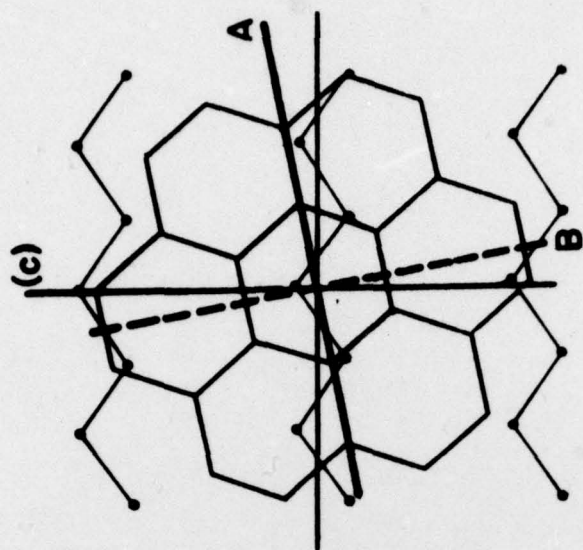
Fig. 1: Spatial arrangement of the heptane chains with respect to the crystallographic system (a,b,c) and to the orthonormal system (x,y,z). The orientation of a vector \vec{V} is defined by ϕ_x, ϕ_y, ϕ_z .

Fig. 2: Zero-field splitting parameters D and E as a function of the $T_1 - S_0$ energy separation of the various sites.

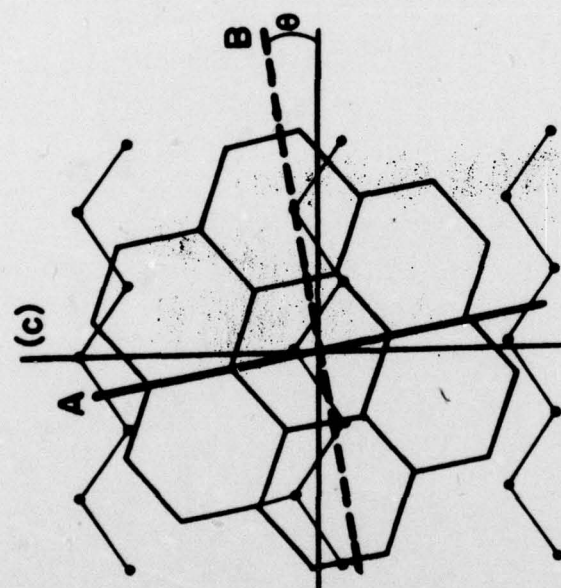
Fig. 3: Orientation of the magnetic axes of molecules in the β , γ and δ sites within the substitutional plane of the lattice which has been taken as the drawing plane.



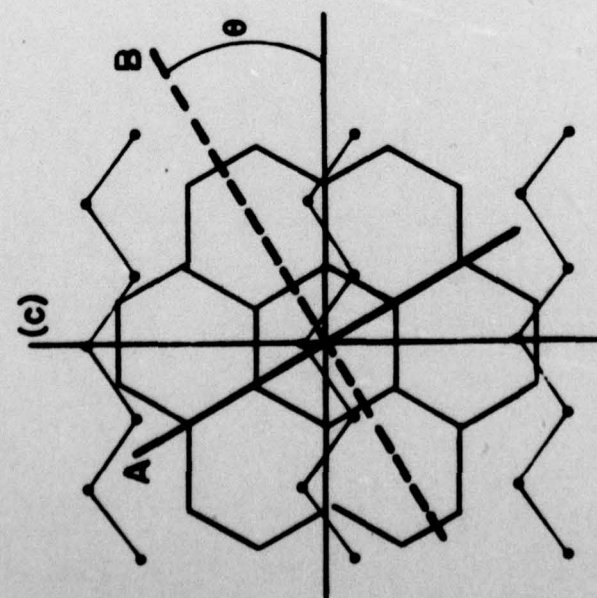




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SITE γ



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